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(54) Process for producing microfine thermoplastic powders

(57) This invention concerns a process for producing microfine thermoplastic powders which can, e.g., be used in the field of surface finishing, as additives for paints and pigments, for coating various materials, including corrosion protection, as well as for modifying certain characteristics of other plastics. The goal and task of this invention is the direct production of microfine thermoplastic powders consisting of spherical particles with a closed surface, having an average particle diameter of $\leq 20\ \mu m$ and a mass weighted particle size distribution of $\leq 50\ \mu m$, by melt dispersing thermoplastics in water, with small additions of dispersing agents and using low agitation speeds. This task is accomplished by adding an alkyl phenol/ethylene oxide adduct, as well as an oxidized polyethylene wax as dispersing agents, and on reaching a temperature which lies at least 30 K above the melting range of the polymer, adding a quantity of an alkaline substance that is equivalent to the acidity of the polyethylene wax to the thermoplastic/water mixture, then agitating at this temperature for 1 to 15 min with an agitation speed of 200 to 800 rpm, and then cooling the dispersion according to known methods to 5 to 20 K below the softening point of the polymer, and finally separating the microfine powder from the water and drying.

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Claims:

1. Process for producing microfine thermoplastic powders consisting of spherical particles with a closed surface, having an average particle diameter of ≤ 20 μm and a mass weighted particle size distribution of ≤ 50 μm, by melt dispersing thermoplastic polymers in an aqueous medium, in the presence of an alkyl phenol/ethylene oxide adduct as the dispersing agent, at pressures up to 4 MPa and temperatures up to 250°C, in a stirred container, using technically readily attainable low agitation speeds of ≤ 600 rpm, without needing to quench the hot emulsion by relaxation in cold water, **characterized in that** an alkyl phenol/ethylene oxide adduct in an amount of 0.2 to 8 wt-% with respect to the mass of the polymer, as well as an oxidized polyethylene wax having a minimum acid number of 16 mg KOH/g of wax, in an amount of 4 to 15 wt-% with respect to the mass of the polymer, are added to the thermoplastic/water mixture as dispersing agents and, on reaching a temperature which lies at least 30K above the melting range of the polymer, adding an amount an alkline substance that is equivalent to the acidity of the oxidized polyethylene wax, with agitation at agitation speeds of ≤ 600 rpm, then continuing to agitate at this temperature for 1 to 15 min with an agitation speed of 200 to 600 rpm, and then cooling the dispersion by known methods to 5 to 20K below the softening point of the polymer and finally separating the microfine powder from the water and drying.
2. Process according to claim 1, **characterized in that** the agitation time amounts to 1 to 15 min, preferably 3 to 10 min, after the addition of the basic substance.
3. Processes according to claims 1 and 2, **characterized in that** thermoplastics are used, whose decomposition temperatures lie at least 30K above their melting range.
4. Process according to claims 1 to 3, **characterized in that** polyethylene and/or ethylene/vinyl acetate copolymers with a vinyl acetate content to 40 wt-% are used as thermoplastics.
5. Process according to claims 1 to 4, **characterized in that** alkali hydroxide, alkaline earth hydroxide, ammonium hydroxide, organic bases or mixtures thereof are used as the alkaline substances.

Area of application of the invention

The invention concerns a process for producing microfine thermoplastic powders, which can be used as such or as aqueous or organic dispersions, in particular for producing printing inks or for obtaining particular surface effects, as well as for coating paper, textiles, metals and other materials, for general surface finishing or corrosion protection, for providing a matte finish to lacquers as well as for modifying the properties of other plastics (e.g. for reducing shrinkage in curing) and for improving the flexibility of thermosetting polymers.

Characteristics of the known technical solutions

The known technical solutions for producing microfine thermoplastic powders using stirred containers as the dispersion device can be characterized as follows:
To obtain fine spherical thermoplastic droplets with a high fraction of < 40 μm particles, which are neither distorted nor agglomerated during the cooling phase, the thermoplastic material is subjected to intensive shear by agitation in aqueous media, under pressure, at temperatures up to 300°C, with the addition of special dispersing agents, e.g. ethylene oxide/propylene oxide block copolymers, metal soaps and organic salts or bases or copolymers of polyethylene that contain ionic groups with acids or caustics, cooling and separating the powder from the water in a known manner, possibly washing, and drying.
A disadvantage of these processes is the high agitation speed, up to > 10000 rpm, which is extraordinarily difficult to control technically, and/or the necessary additions of large amounts of dispersing agent, up to > 100 wt-% (with respect to the amount of polymer being employed), which must then be removed from the thermoplastic powder via complex washing processes.
[illegible] by the technical solution disclosed in DD 206901, but the microfine ther-
[illegible]
[illegible]ssociated and at the same time [illegible]
and the attainable particle size distribution [illegible]

Goal of the invention

The goal of this invention is the development of a technically simple and economically favorable process for producing microfine thermoplastic powder by melt dispersing thermoplastic polymers in water, whereby the resulting thermoplastic particles should be so constituted regarding their geometry and particle size distribution that they are usable for purposes of special applications, e.g. for printing inks or for obtaining special surface effects. Additionally, particular value is attached to the energy balance of the desired process and to the availability of the raw and auxiliary materials that are needed for this purpose.

Description of the nature of the invention

Statement of the objective
It is the task of this invention to develop a process for the direct production of microfine thermoplastic powders consisting of spherical, agglomerate-free particles, with an average particle diameter of ≤ 20 μm and a mass weighted particle size distribution of ≤ 50 μm by melt dispersing thermoplastic polymers in water, using small additions of dispersing agents and using technically readily achievable low agitation speeds.

Characteristics of the invention

It was surprisingly discovered that microfine thermoplastic powders, consisting of spherical particles with a closed surface, having an average particle diameter ≤ 20 μm and a mass weighted particle size distribution of ≤ 50 μm can be produced by melt dispersing thermoplastic polymers in an aqueous medium, at pressures up to 4 MPa and temperatures up to 250°C, in a stirred container, using technically readily achievable, low agitation speeds of ≤ 600 rpm, without requiring quenching of the hot dispersion by relaxation in cold water, if, aside from an alkyl phenol/ethylene oxide adduct in an amount of 0.2 to 8 wt-% with respect to the mass of the polymer being employed, an oxidized polyethylene wax with a minimum acid number of 16 mg KOH/g of wax, in an amount of 4 to 15 wt-% with respect to the mass of the polymer being employed, are added to the system as dispersing agents, and, on reaching a temperature which must be at least 30K above the melting range of the polymer, an amount of alkaline material that is equivalent to the acidity of the oxidized polyethylene wax is added with agitation at speeds of ≤ 600 rpm, then continuing to agitate with an agitation speed of 200 to 600 rpm and subsequently cooling the dispersion to 5 to 20K below the softening point of the polymer by known methods, separating the microfine powder from the water and drying.
Any thermoplastics whose decomposition temperature lies at least 30 K above its melting temperature can be micronized according to this process. Polyolefins and polyolefin copolymers, e.g. polyethylene, polyethylene copolymers, polypropylene, poly-isobutylene, ethylene/vinyl acetate copolymers with a vinyl acetate content up to 40 wt-%, partially saponified ethylene/vinyl acetate copolymers and mixtures of these polymers are particularly suitable.
Problem-free dying and/or pigmentation of the thermoplastics being employed is also feasible during the melt dispersion process.
Solutions of alkali and alkaline earth hydroxides, ammonium hydroxide, organic bases and alkali carbonates can in particular be used as alkaline materials.
A further advantage of the process of this invention consists of the fact that very high yields of over 90 wt-%, with respect to the amount of thermoplastic polymer being employed, of microfine thermoplastic powders having the properties specified by this invention are attainable.
The process of this invention is described in greater detail by means of following examples:

Example embodiments

Example 1:
923 g of high pressure polyethylene (density: 921 kg/m^3) are heated to 200°C with 2000 ml of distilled water, 8g of alkyl phenol/ethylene oxide adduct and 60 g of oxidized polyethylene wax (KOH number: 27.4 mg/g) in a stirred metal autoclave with a usable volume of approximately 4.5 l, at a stirring speed of 70 rpm, whereupon the pressure increases to 1.6 MPa. Once this temperature is reached, the stirring speed is increased to 500 rpm and 11.76 ml of caustic soda solution is metered in through a pressure pipette using ... 1.8 MPa. While maintaining the ...

drawn off
After drying at 55 to 60°C the powder exhibits the following ...

Mesh size (µm)	Remainder (%)
5	97
10	81
20	44
30	23
40	12
50	7

Median d_{50}: 18 µm
Particle size distribution: ≤ 50 µm for 93 wt-%

Example 2:
200 g of ethylene/vinyl acetate copolymer with a vinyl acetate content of 37 wt-% are heated to 180°C with 3000 ml of distilled water, 12 g of alkyl phenol/ethylene oxide adduct and 24 g of oxidized polyethylene wax in a stirred metal autoclave with a usable volume of approximately 4.5 l, with a stirring speed of 60 rpm, whereupon the pressure in the autoclave rises to 1.02 MPa. Once this temperature is reached, the stirring speed is increased to 400 rpm and, using the device described in example 1 at a nitrogen pressure of 1.5 MPa, 10 ml of ammonium hydroxide solution, which contains 41.1 mg of NH_4OH, is metered in, leading to a pressure increase to 1.2 MPa in the autoclave. After stirring for another 15 min at 400 rpm at the aforesaid temperature, the polymer dispersion is cooled to 90°C with further agitation and the powder is treated as described in example 1. Ultrasonic sieving provides the following grain spectrum:

Mesh size (µm)	Remainder (%)
5	98
10	74
20	21
30	5
40	1.2
50	0.4

Median d_{50}: 13.5 µm
Particle size distribution: ≤ 50 µm for 99.6 wt-%

Example 3:
450 g of high pressure polyethylene (density 921 kg/m^3), 2 g of a green phthalocyanine dye, 35g of TiO_2 and 13 g of ZnO are heated to 200°C with 2650 ml of distilled water, 30g of alkyl phenol/ethylene oxide adduct and 60 g of oxidized polyethylene wax (KOH number: 27.4 mg/g), in a stirred metal autoclave with a usable volume of approximately 4.5 l, at a stirring speed of 80 rpm, whereupon the pressure in the autoclave rises to 1.6 MPa. Once this temperature is reached, 15 ml of a 27 wt-% solution of NaOH are added through a pressure pipette using a nitrogen pressure of 2 MPa, while stirring at 80 rpm, whereupon the pressure in the autoclave increases to 1.8 MPa. Subsequently, stirring is continued for 10 min at 550 rpm, at the aforesaid temperature, then the suspension is cooled to 90°C with agitation and the powder is treated as described in example 1. The resulting product is green. Ultrasonic sieving provides the following grain spectrum:

Mass width (µm)	Remainder (%)
10	78
20	44
30	23
40	13
50	8.5

Median d_{50}: 17.5 µm
Particle size distribution: ≤ 50 µm for 91.5 wt-%

Example 4:
500 g of precipitated high pressure polyethylene, which contains 2 g of a red fluorescent pigment pre-added [illegible]

Mesh size (μm)	Remainder(%)
10	70
20	41
30	23
40	15
50	9.5

Median: d_{50}: 16 μm

Particle size distribution: ≤ 50 μm for 90.6 wt-%